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Signed, this 27th day of October, 2009



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[DOCUMENT TITLE] SPECIFICATION

[TITLE OF THE INVENTION] MANUAL TRANSMISSION

[DOCUMENT TITLE] SCOPE OF CLAIM FOR PATENT

1. A manual transmission comprising:

a sliding portion having a hard carbon thin-coated sliding surface of at least one of sliding members sliding with each other under the existence of lubrication oil for manual transmission, wherein the hydrogen content of the hard carbon thin film is 20 atomic percent or less.

2. A manual transmission according to claim 1, wherein the hydrogen content of the hard carbon thin film is 10 atomic percent or less.

3. A manual transmission according to claim 1, wherein the hydrogen content of the hard carbon thin film is 0.5 atomic percent or less.

4. A manual transmission according to any of claims 1 to 3, wherein a surface roughness Ra of a base material before an application of the hard carbon thin film is 0.1µm or less.

5. A manual transmission according to any of claims 1 to 4, wherein the lubricating oil contains the oxygen-containing organic compound and/or an aliphatic amine group compound.

6. A manual transmission according to claim 5, wherein the oxygen-containing organic compound is at least one kind of the compound selected of a group consisting of monovalent or polyalcohols, , carboxylic acids, esters, ethers, ketones, aldehydes, carbonates and derivatives thereof and 0.05 to 3.0 percent thereof is contained on a basis of a total amount of the lubricating oil.

7. A manual transmission according to claim 5 or 6, wherein the aliphatic amine group compound includes hydrocarbon base of C 6 to 30 and 0.05 to 3.0 percent thereof is contained on a basis of a total amount of the lubricating oil.

8. A manual transmission according to any of claims 5 to 7, wherein base of the lubricating oil comprises mineral oil and/or synthetic oil.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD]

[0001] The present invention relates to a fuel saving technology of a manual transmission used for an automobile and in more detail to a manual transmission that is provided with a sliding section that is small in the friction coefficient and excellent in the seizure resistance and wear resistance and can exhibit excellent fuel performance over a long term.

[0002]

[BACKGROUND ART] As to the fuel efficient technology of a manual transmission of an automobile, there is a proposal in which the agitation of lubricating oil by a power transfer is avoided or made very small to inhibit the power transmission efficiency from deteriorating owing to the agitation resistance (for instance, patent literature 1).

[0003]

On the other hand, as to the lubricating oil that is used in such a transmission, a lubricating oil composition in which, to lubrication base oil a boron-L containing ash-L less dispersant, an alkaline-L earth metal base detergent and a sulfur base additive are blended is proposed (patent literature 2). Furthermore, gear oil in which, to base oil that is low in a sulfur content and has predetermined viscosity, primary zinc dithiophosphate, an alkaline earth metal detergent, alkenyl succinic imide having a polybutenyl group having a predetermined molecular weight, a derivative thereof, phosphoric ester amine salt, and a sulfur compound are contained is proposed (patent literature 3).

[0004]

[Patent literature 1] JP-A-10-166877

[Patent literature 2] JP-A-2003-82377

[Patent literature 3] JP-A-11-181463

[0005]

[PROBLEM TO BE SOLVED BY THE INVENTION]

In the manual transmission described in patent literature 1, as described above, the reduction of the agitation resistance of the lubricating oil is studied. However, an improvement in the performance and fuel efficient due to the reduction of the friction of the sliding sections, in particular, the compatibility between a sliding member and the lubricating oil is not studied. Furthermore, as to one that

concerns lubricating oil alone, the lubricating oil is formed into a constitution as shown in examples of the patent literatures 2 and 3 to improve the wear inhibition, the fatigue life and the friction characteristics between a synchronizer ring and a gear cone. However, in the study, the characteristics of the sliding member are not particularly considered to reduce the friction coefficient.

[0006] The invention intends to provide a manual transmission that can reduce the friction coefficient in various kinds of sliding sections in the manual transmission such as bearing sections to improve the seizure resistance and the wear resistance and to reduce the sliding resistance of the respective sections to contribute in improving the fuel efficiency of an automobile.

[0007]

[MEANS FOR THE SOLUTION]

The inventors found that, when one or both of sliding surfaces that slidably contact each other are provided thereon with a hard carbon thin film less in hydrogen content, in the presence of a low-L friction agent composition, the friction coefficient can be largely reduced. Furthermore, the inventors found that, in a sliding member covered with such a hard carbon thin film, in order to realize low friction coefficient and to improve the seizure resistance and the wear resistance, an additive used in the low-L friction agent composition affects to no small extent. Thereby, the invention comes to completion.

[0008] The present invention is made in view of the above findings, and a manual transmission comprises :

a sliding portion having a hard carbon thin-coated sliding surface of at least one of sliding members sliding with each other under the existence of lubrication oil for manual transmission, wherein the hydrogen content of the hard carbon thin film is 20 atomic percent or preferably 10 atomic percent or less, and more preferably 0.5 atomic percent or less.

[0009]

[MODE OF CARRYING OUT THE INVENTION]

In what follows, a low-L friction sliding mechanism and a low-L friction agent composition according to the invention will be more detailed. In the specification, "%" denotes a mass percentage unless otherwise stated.

[0010] Fig. 1 is a sectional view showing an example of a sliding section in an automobile manual transmission according to the invention. A manual transmission 1 according to the invention includes, in a clutch housing, an input shaft 3 supported freely rotatably by two ball bearings 2a and 2b; and a main

shaft 5 supported freely rotatably by a roller bearing 4a and a ball bearing 4b, to the input shaft a 3-speed input gear 3a and a 4-speed input gear 3b, respectively, being rotatably engaged through needle bearings 2c and 2d, a 5-speed input gear 3c being fixed.

[0011] On the other hand, to the main shaft 5, a 1-speed main gear 5a engaging with a gear 3d formed to the input shaft 3 and a 2-speed main gear 5b engaging with a gear 3e of the input shaft 3, respectively, are rotatably engaged through a needle bearing 4c and a needle bearing 4d attached through a 2-speed bush 6a. Furthermore, to the main shaft 5, a 5-speed main gear 5c engaging with a 5-speed input gear 3c of the input shaft 3 is rotatably engaged through a needle bearing 4e attached through a 5-speed bush 6b.

[0012] In the manual transmission 1 according to the invention, in a sliding section between an input shaft 3 and a needle bearing 2c of a 3-L speed input gear 3a and on a surface on a side of the input shaft 3 in a sliding section between an input shaft 3 and a needle bearing 2d of a 4-speed input gear 3b, a hard carbon thin film can be coated. It goes without saying that a hard carbon thin film may be coated on surfaces of the needle bearings 2c and 2d, and hard carbon coat may be formed on both thereof.

[0013] Furthermore, as to the main shaft 5, a hard carbon thin film can be coated on a surface of a main shaft 5 in a sliding section between the main shaft 5 and a needle bearing 4c of the 1-L speed main gear 5a; and on surfaces of bushes 6a and 6b in a sliding section between a 2-L speed bush 6a of the main shaft 5 and a needle bearing 4d and in a sliding section between a 5-L speed bush 6b and a needle bearing 4e. In this case as well, on a surface of the needle bearing 4a, 4b or 4e, or on both of sliding surfaces that contact and slide each other, a hard carbon thin coat can be formed.

[0014] On inner periphery surfaces of the 3-L speed input gear 3a, 4-L speed input gear 3b, 1-L speed main gear 5a, 2-speed main gear 5b and 5-L speed main gear 5c that contact and slide each other with the respective needle bearings 2c, 2d, 4c, 4d and 4e, respectively, a hard carbon coat may be desirably formed as needs arise.

In the above, an example is shown where on five sliding sections in total, that is, the 3-L speed input gear 3a and 4-L speed input gear 3b of the input shaft 3, the 1-L speed main gear 5a of the main shaft 5, the 2-L speed main gear 5b and the 5-L speed main gear 5c, a hard carbon thin film is formed. The hard carbon thin film may be formed on other sliding sections such as the respective sliding

sections of the ball bearings 2a, 2b, 4b and the roller bearing 4a that rotatably support the input shaft 3 and the main shaft 5.

[0015] Here, as the above hard carbon coat, the DLC material constituted mainly of a carbon atom, for example, may be used, the DLC is a bonding state between carbons is made of both of a diamond structure (sp^3 bond) and a graphite bond (sp^2 bond). Specifically, a-C (amorphous carbon) entirely made of carbon element, a-C: H (hydrogen amorphous carbon) containing hydrogen and MeC partially containing a metal element such as titanium (Ti) or molybdenum (Mo) can be cited.

[0016] In addition, when the hydrogen content in the hard carbon thin film increases, the friction coefficient increases. Therefore it is necessary to set the upper limit of the hydrogen content to 20 atomic % in the present invention, but for sufficiently lowering the friction coefficient at sliding in the lubricating oil and further securing the stable sliding characteristic, it is lowered to preferably 10 atomic % or less or more preferably 0.5atomic % or less.

[0017] And such a hard carbon thin film having the low hydrogen content can be obtained by forming a film by a sputtering process or an ion plating process, that is, by a PVD process substantially not using hydrogen or hydrogen-containing compound.

In this case, for reducing a hydrogen amount in the coating, it is preferable to not only use the gas not containing the hydrogen at film forming, but also, just in case, to form a film after sufficiently cleaning on the substrate surface.

[0018] In addition, the surface roughness of the substrate after coated with the hard carbon thin film has a big impact on the roughness of the membrane surface after filming because of the extremely thin hard carbon thin film. Therefore, it is preferable to the surface roughness Ra (average roughness in the center line) is 0.1 μ m or less. That is, in a case where the surface roughness Ra is rough exceeding 0.1 μ m, a projector due to the roughness of the membrane surface increases a local contact surface pressure to the opponent to increase the probability of involving a crack of the membrane.

[0019] Next, a lubricating oil used in a manual transmission of the present invention will be explained in detail. As the lubricating oil used in a manual transmission of the present invention, it is preferable to use oil formed by containing an oxygen-containing organic compound and/or an aliphatic amine group compound in a base oil, and the low friction characteristics can be achieved by interposing such a lubricating oil between the sliding surfaces

coated with the hard carbon thin film.

[0020] As the above-mentioned medium there is particularly preferably employed a lubricating oil base oil (a base oil of the lubricating oil). Such lubricating oil base oil is not particularly limited and any ordinary base oil, either mineral oil type or synthetic type, for lubricant composition can be employed.

Examples of the lubricating oil base oil of mineral oil type include a product formed by subjecting a lubricant fraction, obtained as a result of atmospheric distillation or vacuum distillation of crude oil, to at least one of solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, hydrotreating and wax isomerization, particularly a base oil subjected to hydrocracking, hydrotreating or wax isomerization. Among such products, there is preferred a mineral oil obtained by hydrotreating or hydrocracking, or an isoparaffinic mineral oil obtained by isomerization of GTL (gas-to-liquid) wax by a Fischer-Tropsch process or of normal paraffin-rich wax obtained in a dewaxing step of lubricant oil.

[0021] Examples of the lubricating oil base oil of synthetic type include an alkylnaphthalene, an alkylbenzene, a polybutene and a hydrogenated product thereof; a poly- α -olefin such as a 1-octene oligomer, a 1-decene oligomer, an ethylene propylene oligomer or a hydrogenated product thereof; an isobutene oligomer and a hydrogenated product of isobutene oligomer; isoparaffin, alkylbenzene, alkylnaphthalene, diester (for example, trimethylpropane ester such as trimethylpropane caprylate, trimethylpropane pelargonate, trimethylpropane pelargonate, trimethylpropane isostearinate and the like; and pentaerythritol ester such as pentaerythritol-2-ethylhexanoate, pentaerythritol pelargonate), polyoxalkylene glycol, dialkylidiphenyl ether, polyphenyl ether and the like; and mixtures of these. Preferable examples of the synthetic lubricating oil base oil are poly- α -olefin such as 1-octene oligomer, 1-decene oligomer and the like, and hydrogenated product thereof.

[0022] In regard to the base oil used in the lubricating oil for a manual transmission for the present invention, in addition to the use of the lubricating oil base oil of mineral oil type or the lubricating oil base oil of synthetic type either singly or as a mixture, it is also possible to use a mixture of two or more kinds of the base oil of mineral oil type or the base oil of synthetic type. Also in such mixture, a mixing ratio of two or more kinds of the base oils is not particularly restricted and can be selected arbitrarily.

[0023] A sulfur amount in the base oil is not limited in particular, but the sulfur amount is preferably 0.2% or less on a basis of a total amount of the base oil, more preferably 0.1% and furthermore preferably 0.05%. In particular, since the sulfur amount in the hydro-refining mine oil or the synthetic base oil is 0.005 % or less or does not contain the sulfur substantially (5ppm or less), it is preferable to use it as the base oil.

[0024] A total aromatic content of the lubricating oil base oil is not particularly restricted, but for maintaining long-term low friction characteristics as the lubricating oil in the transmission for an automobile, it is preferably 15 % or less, more preferably 10 % or less and further preferably 5 %. A total aromatic content in the lubricating oil base oil exceeding 15 % results in an inferior stability to oxidation and is undesirable. The "total aromatic content" means a content of an aromatic fraction measured according to ASTM D2549.

[0025] Also the lubricating oil base oil is not particularly restricted in a kinetic viscosity thereof, but in case of use as a lubricant composition for a transmission, a kinetic viscosity at 100°C is preferably 2 mm²/s or higher, and more preferably 3 mm²/s or higher. Also an upper limit is preferably 20 mm²/s or less, more preferably 10 mm²/s or less and particularly preferably 8 mm²/s or less. A lubricating oil base oil with a kinetic viscosity at 100°C of 2 mm²/s or higher allows to obtain a composition capable of sufficient oil film formation, an excellent lubricating property and a smaller evaporation loss of the base oil under a high temperature condition. On the other hand, a kinetic viscosity at 100°C of 20 mm²/s or less reduces a fluid resistance, thereby allowing to obtain a composition with a smaller frictional resistance in a lubricated site. If the kinetic viscosity is less than 2 mm²/s, there is the possibility that a sufficient frictional resistance can be obtained while a vaporizing characteristics is inferior, which is not preferable. If the kinetic viscosity exceeds 20 mm²/s, there is the possibility that a low friction characteristics is difficult to be exhibited while a low temperature characteristics are degraded, which are not preferable. In the present invention, a mixture which are prepared by freely mixing two or more base oils selected from the above-mentioned base oils can be used, in which the base oils having the kinetic viscosity (as a single base oil) other than the above-mentioned can be also used as far as the base oils have a kinetic viscosity at 100°C which viscosity is within the above-mentioned preferable range.

[0026] Furthermore, a viscosity index of the lubricating oil base oil is not

2,2-^L dimethyl-^L 3-^L pentanol, 2,3-^L dimethyl-^L 3-^L pentanol, 2,4-^L dimethyl-^L 3-^L pentanol, 4,4-^L dimethyl-^L 2-^L pentanol, 3-^L methyl-^L 1-^L hexanol, 4-^L methyl-^L 1-^L hexanol, 5-^L methyl-^L 1-^L hexanol, 2-^L ethyl(pentanol), octanol (1-^L octanol, 2-^L octanol, 3-^L octanol, 4-^L methyl-^L 3-^L heptanol, 6-^L methyl-^L 2-^L heptanol, 2-^L ethyl-^L 1-^L hexanol, 2-^L propyl-^L 1-^L pentanol, 2,4-^L trimethyl-^L 1-^L pentanol, 3,5-^L dimethyl-^L 1-^L hexanol, 2-^L methyl-^L 1-^L heptanol, 2,2-^L dimethyl-^L 1-^L hexanol, nonanol (1-^L nonanol, 2-^L nonanol, 3,5,5-^L trimethyl-^L 1-^L hexanol, 2,6-^L dimethyl-^L 4-^L heptanol, 3-^L ethyl-^L 2,2-^L dimethyl-^L 3-^L pentanol, 5-^L methyl(octanol, etc.), decanol (1-^L decanol, 2-^L decanol, 4-^L decanol, 3,7-^L dimethyl-^L 1-^L octanol, 2,4,6-^L trimethylheptanol, etc.), undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol (stearyl alcohol, etc.), nonadecanol, eicosanol, heneicosanol, tricosanol, tetracosanol; monohydric alkenyl alcohols having from 2 to 40 carbon atoms (in which the alkenyl group may be linear or branched and the double bond may be in any desired position) such as ethenol, propenol, butenol, hexenol, octenol, decenol, dodecenol, octadecenol (oleyl alcohol, etc.); monohydric (alkyl) ^L cycloalkylalcoholshavingfrom 3 to 40 carbon atoms (in which the alkyl group may be linear or branched, and the alkyl group and the hydroxyl group may be in any desired position) such as cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, methylcyclopentanol, ^L methylcyclohexanol, dimethylcyclohexanol, ethylcyclohexanol, propylcyclohexanol, butylcyclohexanol, dimethylcyclohexanol, cyclopentylmethanol, cyclohexylethanol (1-^L cyclohexylethanol, 2-^L cyclohexylethanol, etc.), cyclohexylethanol, cyclohexylpropanol (3-^L cyclohexylpropanol, etc.), cyclohexylbutanol (4-^L cyclohexylbutanol, etc.) butylcyclohexanol, 3,3,5,5-^L tetramethylcyclohexanol; (alkyl) aryl alcohols (in which the alkyl group may be linear or branched, and the alkyl group and the hydroxyl group may be in any desired position) such as phenyl alcohol, methylphenyl alcohol (o-^L cresol, m-^L cresol, p-^L cresol), cresol, ethylphenyl alcohol (3-^L methyl-^L 6-^L tert-^L butylphenyl alcohol, etc.), dimethylphenyl alcohol, diethylphenyl alcohol, dibutylphenyl alcohol (2,6-^L di-^L tert-^L butylphenyl alcohol, 2,4-^L di-^L tert-^L butylphenyl alcohol, etc.), dibutylmethylphenyl alcohol (2,6-^L di-^L tertbutyl-^L 4-^L methylphenyl alcohol, etc.), dibutylethylphenyl alcohol (2,6-^L di-^L tert-^L butyl-^L 4-^L ethylphenyl alcohol, etc.), tributylphenyl

alcohol (2,4,6-*tri-tert-butylphenyl* alcohol, etc.), naphthol (*a-naphthol*, *b-naphthol*, etc.), *di-*n*-butyl-naphthol* (2,4-*di-tert-butyl-a-naphthol*, etc.); 6-(4-*hydroxy-3,5-di-tert-butylanilino*)-2,4-*bis*-(*n-octylthio*)-1,3,5-*tri*azine, and their mixtures.

[0030] Of those, more preferred are linear or branched alkyl or alkenyl alcohols having from 12 to 18 carbon atoms such as *oleyl* alcohol and *stearyl* alcohol, in that they may more effectively lower the friction of the sliding surfaces formed of the hard carbon thin film coated sliding member and any other member and that they are poorly volatile and therefore may exhibit their friction-reducing effect even at high temperature conditions (for example, sliding condition in an internal combustion engine).

[0031] Dialcohols (1-2) are concretely those having two hydroxyl groups in the molecule, including, for example, alkyl or alkenyldiols having from 2 to 40 carbon atoms (in which the alkyl or alkenyl group may be linear or branched, the double bond of the alkenyl group may be in any desired position, and the hydroxyl group may also be in any desired position) such as *ethylene glycol*, *diethylene glycol*, *polyethylene glycol*, *propylene glycol*, *dipropylene glycol*, *polypropylene glycol*, *neopentyl glycol*, *1,3-propanediol*, *1,4-butanediol*, *1,2-butanediol*, *2-methyl-1,3-propanediol*, *1,5-pentanediol*, *2-ethyl-2-methyl-1,3-propanediol*, *1,6-hexanediol*, *2-ethyl-2-methyl-1,3-propanediol*, *2-methyl-2,4-pentanediol*, *1,7-heptanediol*, *2-methyl-2-propyl-1,3-propanediol*, *2,2-diethyl-1,3-propanediol*, *1,8-octanediol*, *1,9-nonanediol*, *2-butyl-2-ethyl-1,3-propanediol*, *1,10-decanediol*, *1,11-undecanediol*, *1,12-dodecanediol*, *1,13-tridecanediol*, *1,14-tetradecanediol*, *1,15-heptadecanediol*, *1,16-hexadecanediol*, *1,17-heptadecanediol*, *1,18-octadecanediol*, *1,19-nonadecanediol*, *1,20-icosadecanediol*; (alkyl) *cycloalkenediols* (in which the alkyl group may be linear or branched, and the alkyl group and the hydroxyl group may be in any desired position) such as *cyclohexanediol*, *methylcyclohexanediol*; *dihydric* (alkyl) *aryl* alcohols having from 2 to 40 carbon atoms (in which the alkyl group may be linear or branched, and the alkyl group and the hydroxyl group may be in any desired position) such as *benzenediol* (*catechol*, etc.), *methylbenzenediol*, *ethylbenzenediol*, *butylbenzenediol* (*p-tert-butylcatechol*, etc.), *di-*n*-butylbenzenediol* (4,6-*di-tert-butylresorcinol*, etc.), *4,4'-thiobis* (3-methyl-6-*tert-butylphenol*), *4,4'-butyldienebis* (3-methyl-6-*tert-butylphenol*),

2,2'-l-methylenebis l (4-l-methyl-l-6-l-tert-l-butylphenol),
 2,2'-l-thiobis l (4,6-l-di-l-tertbutylresorcinol),
 2,2'-l-methylenebis l (4-l-ethyl-l-6-l-tert-l-butylphenol),
 4,4'-l-methylenebis l (2,6-l-di-l-tert-l-butylphenol), l 2,2'-(3,5-l-dilert-l-butylhydroxy) l propane,
 4,4'-l-cyclohexylidenebis l (2,6-l-di-l-tert-l-butylphenol);
 p-l-tert-l-butylphenol/l-formaldehyde condensate,
 p-l-tert-l-butylphenol/l-acetaldehyde condensate, and their mixtures.

[0032] Of those, preferred are ethylene glycol, propylene glycol, neopentyl glycol, 1,4-l-butanediol, 1,5-l-pentanediol, neopentyl glycol, 1,6-l-hexanediol, 2-l-methyl-l-2,4-l-pentanediol, 2-l-ethyl-l-2-l-methyl-l-1,3-l-propanediol, 1,7-l-heptanediol, 1,8-l-octanediol, 1,9-l-nonanediol, 1,10-l-decanediol, 1,11-l-undecanediol and 1,12-l-dodecanediol, in that they may more effectively lower the friction at the sliding surfaces of the hard carbon thin film coated sliding member and of any member. In addition, high-l-molecular-l-weight hindered alcohols having a molecular weight of at least 300, preferably at least 400 such as 2,6-di-l-tert-l-butyl-l-4-(3,5-l-di-l-tert-l-butyl-l-4-l-hydroxybenzyl) phenyl alcohol are also preferred in that they are hardly volatile even at high temperatures (for example, under sliding condition in internal-l-combustion engines) and are highly resistant to heat, and they can well exhibit their friction-l-reducing effect and can impart excellent antioxidation stability to lubricating oil.

[0033] Tri- and higher polyalcohols (1-3) are concretely those having three or more hydroxyl groups. In general, tri- to deca-l-alcohols, preferably tri- to hexa-l-alcohols are used. Examples of these components are trimethylolalkanes such as glycerin, trimethylolmethane, trimethylolpropane, trimethylolbutane; as well as erythritol, pentaerythritol, 1,2,4-l-butanetriol, 1,3,5-l-pentanetriol, 1,2,6-l-hexanetriol, 1,2,3,4-l-butanetetrol, sorbitol, adonitol, arabitol, xylitol, mannitol; and their polymers or condensates (e.g., glycerindimers to octamers such as diglycerin, triglycerin, tetraglycerin; trimethylolpropane dimmers to octamers such as ditrimethylolpropane; pentaerythritol dimers to tetramers such as dipentaerythritol; sorbitan; condensates such as sorbitol/l-glycerin condensate (including intramolecular condensates, intermolecular condensates, and self-l-condensates)).

[0034] Saccharides such as xylose, arabitol, ribose, rhamnose, glucose, fructose,

galactose, mannose, sorbose, cellobiose, mannose, isomaltose, trehalose and sucrose are also usable.

[0035] Of those, more preferred are tri to hexa-^L alcohols such as glycerin, trimethylolalkanes (e.g., trimethylethane, trimethylpropane, trimethylbutane), pentaerythritol, 1,2,4-^L butanetriol, 1,3,5-^L pentanetriol, 1,2,6-^L hexanetriol, 1,2,3,4-butanetriol, sorbitol, sorbitan, sorbitol/^L glycerin condensate, adonitol, arabitol, xylitol, mannitol, and their mixtures; and even more preferred are glycerin, trimethylethane, trimethylpropane, pentaerythritol, sorbitan and their mixtures. Especially preferred are polyalcohols having an oxygen content of at least 20 %, preferably at least 30 %, more preferably at least 40 %. Polyalcohols that are higher than hexa-^L alcohols will too much increase the viscosity.

[0036] Further, the alkylene oxide additive (1-4) is an alkylene oxide additive of alcohols selected from (1-1 to 1-3), and specially alkylene oxide of C 2 to 6, preferably C 2 to 4, the polymer or copolymer is added to the alcohols and hydroxyl group of alcohols are haldorokarubi-etherified or haldorokarubi-esterified. Alkylene oxide of C 2 to 6, ethylene oxide, propylene oxide, 1,2-epoxy butane (α -butylene oxide), 2,3 epoxy butane (β -butylene oxide), 1, 2-epoxy-1-methyl propane, 1-2-epoxy heptane, 1, 2 epoxy hexane and the like are exemplified. Among them, from a viewpoint of excellent low friction properties, ethylene oxide, propane oxide and butylene oxide are preferable.

[0037] In a case of using two or more kinds of alkylene oxide, there is no limit to polymer form of oxy alkylene group, and random copolymer or block copolymer may be allowed. Upon adding alkylene oxide to poly alcohol having 2 to 6 pieces of hydroxyl group, it may add to all hydroxyl group or a part of hydroxyl group.

[0038] Examples of carboxylic acids (II) are mentioned below:

Aliphatic monocarboxylic acids (fatty acids)(II-1);

Aliphatic polycarboxylic acids^L (II-^L 2);

Carbon-^L cyclic carboxylic acids (II-^L 3);

Heterocyclic carboxylic acids (II-^L 4); and

Mixtures of two or more selected from the above four kinds of carboxylic acids^L (II-5).

[0039] Aliphatic monocarboxylic acids (fatty acids) (II-^L 1) are concretely those having one carboxyl group in the molecule, including, for example, saturated

aliphatic monocarboxylic acids having from 1 to 40 carbon atoms (in which the saturated aliphatic structure may be linear or branched) such as methanoic acid, ethanoic acid (acetic acid), propanoic acid (propionic acid), butanoic acid (butyric acid, isobutyric acid, etc.), pentanoic acid (valeric acid, isovaleric acid, pivalic acid, etc.), hexanoic acid (caproic acid, etc.), heptanoic acid, octanoic acid (caprylic acid, etc.), nonanoic acid^L (pelargonic acid, etc.), decanoic acid, undecanoic acid, dodecanoic acid (lauric acid, etc.), tridecanoic acid, tetradecanoic acid (myristic acid, etc.), pentadecanoic acid, hexadecanoic acid (palmitic acid, etc.), heptadecanoic acid, octadecanoic acid (stearic acid, etc.), nonadecanoic acid, eicosanoic acid, heneicosanoic acid, docosanoic acid,tricosanoic acid, tetracosanoic acid, pentacosanoic acid, hexacosanoic acid, heptacosanoic acid, octacosanoic acid, nonacosanoic acid, triacontanoic acid; and unsaturated aliphatic monocarboxylic acids having from 1 to 40 carbon atoms (in which the unsaturated aliphatic structure maybe linear or branched, and the unsaturated bond may be in any desired position) such as propenoic acid (acrylic acid, etc.), propynoic acid (propioic acid, etc.), butenoic acid (methacrylic acid, crotonic acid, isocrotonic acid, etc.), pentenoic acid, hexenoic acid, heptenoic acid, octenoic acid, nonenoic acid, decenoic acid, undecenoic acid, dodecenoic acid, tridecenoic acid, tetradecenoic acid, pentadecenoic acid, hexadecenoic acid, heptadecenoic acid, octadecenoic acid (oleic acid, etc.), nonadecenoic acid, eicosenoic acid, heneicosenoic acid, docosenoic acid,tricosenoic acid, tetracosenoic acid, pentacosenoic acid, hexacosenoic acid, heptacosenoic acid, octacosenoic acid, nonacosenoic acid, triacontenoic acid. [0040] Aliphatic polycarboxylic acids (II-2) include saturated or unsaturated aliphatic dicarboxylic acids having from 2 to 40 carbon atoms (in which the saturated aliphatic or unsaturated aliphatic structure maybe linear or branched, and the unsaturated bond may be in any desired position) such as ethane-^L-diacid (oxalic acid), propane-^L-diacid (malonic acid, etc.), butane-^L-diacid (succinic acid), methylmalonic acid, etc.), pentane-^L-diacid (glutaric acid, ethylmalonic acid, etc.), hexane-^L-diacid (adipic acid, etc.), heptane-^L-diacid (pimelic acid, etc.), octane-^L-diacid (suberic acid, etc.), nonane-^L-diacid (azelaic acid, etc.), decane-^L-diacid (sebacic acid, etc.), propene-^L-diacid, butene-^L-diacid (maleic acid, fumaric acid, etc.), pentene-^L-diacid (citraconic acid, mesaconic acid, etc.), hexene-^L-diacid, heptene-^L-diacid, octene-^L-diacid, nonene-^L-diacid, decene-^L-diacid; saturated or unsaturated tricarboxylic acids (in which the saturated aliphatic or unsaturated

aliphatic structure may be linear or branched, and the unsaturated bond may be in any desired position) such as propanetricarboxylic acid, butane-^L-tricarboxylic acid, pentane-^L-tricarboxylic acid, hexane-^L-tricarboxylic acid, heptane-^L-tricarboxylic acid, octane-^L-tricarboxylic acid, nonane-^L-tricarboxylic acid, decane-^L-tricarboxylic acid; and saturated or unsaturated tetracarboxylic acids (in which the saturated aliphatic or unsaturated aliphatic structure may be linear or branched, and the unsaturated bond may be in any desired position).

[0041] Carbon-cyclic carboxylic acids (II-3) are concretely those having one or more carboxyl groups in the carbocyclic molecule, including, for example, naphthene ring-^L having, mono, di, tri or tetracarboxylic acids having from 3 to 40 carbon atoms (in which the alkyl or alkenyl group, if any therein, maybe linear or branched, and the double bond, if any therein, may be in any desired position, and the number and the position of the substituents are not defined) such as cyclohexane-^L monocarboxylic acid, methylcyclohexane-^L monocarboxylic acid, ethylcyclohexane-^L monocarboxylic acid, propylcyclohexane-^L monocarboxylic acid, butylcyclohexane-^L monocarboxylic acid, pentylcyclohexane-^L monocarboxylic acid, hexylcyclohexane-^L monocarboxylic acid, heptylcyclohexane-^L monocarboxylic acid, octylcyclohexane-^L monocarboxylic acid, cycloheptane-^L monocarboxylic acid, cyclooctane-^L monocarboxylic acid, trimethylcyclopentane-^L dicarboxylic acid (camphor acid, etc.); aromatic monocarboxylic acids having from 7 to 40 carbon atoms such as benzenecarboxylic acid (benzoic acid), methylbenzenecarboxylic acid (toluic acid, etc.), ethylbenzenecarboxylic acid, propylbenzenecarboxylic acid, benzenedicarboxylic acid (phthalic acid, isophthalic acid, terephthalic acid, etc.), benzenetricarboxylic acid^L (trimellitic acid, etc.), benzenetetracarboxylic acid^L (pyromellitic acid^L etc.), naphthalenecarboxylic acid (naphthoic acid, etc.); mono, di, tri or tetracarboxylic acids having an aryl group with from 7 to 40 carbon atoms (in which the alkyl or alkenyl group, if any therein as a substituent, may be linear or branched and the double bond, if any therein, may be in any desired position, and the number and the position of the substituents are not defined) such as phenylpropanoic acid (hydroatropic acid), phenylpropenoic acid (atropic acid, cinnamic acid, etc.), salicylic acid, alkylsalicylic acid having one or more alkyl groups with from 1 to 30 carbon atoms.

[0042] Heterocyclic carboxylic acids (II-^L 4) are concretely those having one or more carboxyl groups in the molecule, including, for example, those having from

5 to 40 carbon atoms such as furanecarboxylic acid, thiophenecarboxylic acid, pyridinecarboxylic acid (nicotinic acid, isonicotinic acid, etc.).

[0043] Examples of ethers (II) are mentioned below:

Saturated or unsaturated aliphatic ethers(III-1);

Aromatic ethers (III-2);

Cyclic ethers (III-3);

Polyalcoholic esters (III-4); and

Mixtures of two or more selected from the above three kinds of ethers (III-5) .

[0044] Saturated or unsaturated aliphatic ethers(aliphatic monoethers) are concretely saturated or unsaturated aliphatic ethers (III-1) having from 1 to 40 carbon atoms (in which the saturated or unsaturated aliphatic structure may be linear or branched, and the unsaturated bond may be in any desired position) such as dimethyl ether, diethyl ether, di-¹-n-¹-propyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether, di-¹-n-¹-amyl ether, disoamyl ether, dihexyl ether, diheptyl ether, dioctyl ether, dinonyl ether, didecyl ether, didodecyl ether, ditridecyl ether, ditetradecyl ether, dipentadecyl ether, ¹-dihexadecyl ether, diheptadecyl ether, dioctadecyl ether, dinonadecyl ether, dieicosyl ether, methyl ethyl ether, methyl n-¹-propyl ether, methyl isopropyl ether, methyl isobutyl ether, methyl tert-¹-butylether, methyl n-¹-amyl ether, methyl isoamyl ether, ethyl n-¹-propyl ether, ethyl isopropyl ether, ethyl isobutyl ether, ethyl tert-¹-butyl ether, ethyl n-¹-amyl ether, ethyl isoamyl ether, dimethyl ether, diallyl ether, methyl vinyl ether, methyl allyl ether, ethyl vinyl ether, ethyl allyl ether.

[0045] Concretely, aromatic ethers (III-2) include, for example, anisole, phenetole, phenyl ether, benzyl ether, phenyl benzyl ether, a-¹-naphthyl ether, b-¹-naphthyl ether, polyphenyl ether, perfluoroether; and these may have a saturated or unsaturated group (in which the saturated or unsaturated group may be linear or branched, and the unsaturated bond may be in any desired position, and the number and the position of the substituents are not defined) . Preferably, these are liquid under the service condition thereof, especially at room temperature.

[0046] Concretely, cyclic ethers (III-3) are those having from 2 to 40 carbon atoms, including, for example, ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran, tetrahydropyran,

dioxane, glycidyl ether; and these may have a saturated or unsaturated group, a carbon ring, or a saturated or unsaturated aliphatic group-^L having carbon ring (in which the saturated or unsaturated group may be linear or branched, and the unsaturated bond may be in any desired position, and the number and the position of the substituents are not defined).

[0047] Examples of esters are mentioned below:

4.1 Esters of aliphatic monocarboxylic acids (fatty acids) :

4.2 Esters of aliphatic polycarboxylic acids ;

4.3 Esters of carbon-^L cyclic carboxylic acids;

4.4 Esters of heterocyclic carboxylic acids;

4.5 Mixtures of any compounds selected from the above five kinds of esters .

4.6 Esters of the above 4.1 to 4.5 may be complete esters in which the hydroxyl group and the carboxyl group are all esterified, or partial esters in which the hydroxyl group or the carboxyl group partially remains as such.

[0048] The ester of aliphatic monocarboxylic acids (fatty acids) (4.1) is an ester of one or more selected from the above-^L mentioned aliphatic monocarboxylic acids^L (fatty acids) and one or more selected from the above-^L mentioned mono, di, tri or higher polyalcohols . Examples of the esters are aliphatic monocarboxylic acids. Concrete examples of the esters are glycerin monooleate, glycerin dioleate, sorbitan monooleate, sorbitan dioleate, and the like.

[0049] As esters (4-1) other than such aliphatic acid ester base ashless friction modifier, aliphatic esters having straight-chain or branched hydrocarbons of C 1 to 5 of C31 to 40 are exemplified, and esters composed of aliphatic acids having such a hydrocarbon and aliphatic monoalcohols or aliphatic polyalcohols are exemplified. Among them, the esters having kinetic viscosity of 1 to 100mm² at 100°C can be used as lubricating oil base oil, and normally can be distinguished from the aliphatic acid ester ashless friction modifier. As these examples, tri or more polyols such as trimethyl propane caprylate, trimethyl propane pelargonate, pentaerythritol 2-ethylhexanoate, and pentaerythritol pelargonate of C3 to 40 preferably C4 to 18, more preferably 4 to 12, tri or more polyols having a neopentyl structure, one kind, two kinds or more of single esters selected of monocarboxylate acid of C1 to 40, preferably C 4 to 18, more preferably C6 to 12, polyol esters such as complex esters and the mixtures, or esters added by alkylene oxide are exemplified. They may be complete esters by esterifying all of hydroxyl groups or carboxyl groups or partial esters where hydroxyl groups or the carboxyl groups partially remain, but the complete esters are preferable and

the hydroxyl bases are normally equal to or less than 100mgKOH/g, preferably 50mgKOH/g, more preferably 10mgKOH/g. Among them, the esters having kinetic viscosity of preferably 2 to 60mm²/s, more preferably 3 to 50mm²/s at 100°C can be used as lubricating oil base oil.

[0050] The ester of aliphatic polycarboxylic acids (4.2) is an ester of one or more selected from the above-mentioned aliphatic polycarboxylic acids and one or more selected from the above-mentioned mono, di, tri or higher polycarboxylic acids. Its preferred examples are diesters of one or more polycarboxylic acid selected from dicarboxylic acids having from 2 to 40, preferably from 4 to 18, more preferably from 6 to 12 carbon atoms, and one or more selected from monoalcohols having from 4 to 40, preferably from 4 to 18, more preferably from 6 to 14, such as dibutyl maleate, ditridecyl glutamate, di-2-ethylhexyl adipate, diisodecyladipate, di-2-ethylhexyl sebacate, and copolymers of these diesters (e.g., dibutyl maleate) and poly- α -olefins having from 4 to 16 carbon atoms; and esters of α -olefin adducts to acetic anhydride or the like, and alcohols having from 1 to 40 carbon atoms. Among them, the esters having kinetic viscosity of 1 to 100mm²/s at 100°C can be used as lubricating oil base oil.

[0051] The ester of carbon- α -cyclic carboxylic acids (4.3) is an ester of one or more selected from the above-mentioned carbon- α -cyclic carboxylic acids, and one or more selected from the above-mentioned mono, di, tri or higher polycarboxylic acids. Its preferred examples are aromatic carboxylic acid ester such as phthalic acid ester, trimellitic acid ester, pyromellitic acid ester, salicylic acid ester. Among them, the esters having kinetic viscosity of 1 to 100mm²/s at 100°C can be used as lubricating oil base oil.

[0052] The ester of heterocyclic carboxylic acids (4.4) is an ester of one or more selected from the above-mentioned heterocyclic carboxylic acids, and one or more selected from the above-mentioned mono, di, tri or higher polycarboxylic acids. Among them, the esters having kinetic viscosity of 1 to 100mm²/s at 100°C can be used as lubricating oil base oil.

[0053] As alkylene oxide additives (4-5) of alcohols or esters, esters by adding alkylene oxides to one or more kinds selected of the above mono or more polycarboxylic acids or esters by adding the alkylene oxides to the above (4-1 to 4.4) esters are exemplified. Among them, the esters having kinetic viscosity of 1 to 100mm²/s at 100°C can be used as lubricating oil base oil.

[0054] Derivatives of the above-mentioned organic oxygen-containing organic

compounds can be used like the oxygen-^L-containing organic compounds. Examples of the derivatives are nitrogen-^L-containing compounds, sulfur or sulfur containing compound, boron-^L-containing compound, halogen elements or halogen element-^L-containing compounds, metal elements or metal-^L-containing compounds (organic or inorganic ones), and compounds obtained by reacting alkylene oxide; however, the derivatives are not limited to the above ones. The derivatives concretely include, for example, compounds prepared by sulfidizing one selected from the above-^L-mentioned alcohols, carboxylic acids, esters and ethers, ketones, aldehydes and carbonates; compounds prepared by halogenating (fluorinating, chlorinating) the same one; its reaction products with acids, such as sulfuric acid, nitric acid, boric acid, phosphoric acid, or their esters or metal salts; and its reaction products with metals, metal-^L-containing compounds or amine compounds. Of those, preferred are reaction products of one or more selected from alcohols and carboxylic acids and their derivatives, with amine compounds (e.g., Mannich reaction products, acylated products, amides).

The amine compounds as referred to herein include ammonia, monoamines, diamines, and polyamines. More concretely, their examples are ammonia; alkylamines having an alkyl group with from 1 to 30 carbon atoms (in which the alkyl group may be linear or branched) such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, dinonylamine, didodecylamine, ditridecylamine, diundecylamine, didodecylamine, dihexadecylamine, diheptadecylamine, dioctadecylamine, ethylpropylamine, methylbutylamine, and propylbutylamine; alkenylamines having an alkenyl group with from 2 to 30 carbon atoms (in which the alkenyl group may be linear or branched) such as ethenylamine, propenylamine, butenylamine, octenylamine, and oleylamine; alkanolamines having an alkanol group with from 1 to 30 carbon atoms (in which the alkanol group may be linear or branched) such as

methanolamine, ethanolamine, propanolamine, butanolamine, pentanolamine, hexanolamine, heptanolamine, octanolamine, nonanolamine, methanoldiethanolamine, methanolpropanolamine, methanolbutanolamine, ethanolpropanolamine, ethanolbutanolamine, and propanolbutanolamine; alkylenediamines having an alkylene group with from 1 to 30 carbon atoms, such as methylenediamine, ethylenediamine, propylenediamine, and butylenediamine; polyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine; compounds derived from the above-mentioned monocations, diamines or polyamines and further having an alkyl or alkenyl group with from 8 to 20 carbon atoms, such as undecyldiethyamine, undecyldiethanolamine, dodecyldipropanolamine, oleyldiethanolamine, oleylpropylenediamine, stearyltriethylenepentamine; heterocyclic compounds such as N-Hydroxyethyl/oleylimidazole; alkylene oxide adducts of these compounds; and their mixtures.

[0055] Of those nitrogen-containing compounds, preferred are aliphatic amines having an alkyl or alkenyl group with from 10 to 20 carbon atoms (these may be linear or branched) such as decylamine, dodecylamine, tridecylamine, heptadecylamine, octadecylamine, oleylamine and stearylamine. Of the derivatives of these oxygen-containing organic compounds, preferred are amides of carboxylic acid having 8 to 20 carbon atoms, of the above-mentioned aliphatic monocarboxylic acids (fatty acids) such as oleic amide.

[0056] Examples of the aliphatic amine compound in the low-⁻¹ friction agent composition of the present invention are aliphatic amine compounds each having C6-C30 straight or branched hydrocarbon chains or groups, preferably C8-C24 straight or branched hydrocarbon chains, more preferably C10-C20 straight or branched hydrocarbon chains. When the carbon number of the hydrocarbon chain is not within the range of 6 to 30, there arises a possibility that the lubricating oil may not produce a sufficient friction reducing effect as expected. It is a matter of course that other hydrocarbon groups are had if straight or branched aliphatic hydrocarbon groups within the above carbon number range.

[0057] Specific examples of the C6-C30 straight or branched hydrocarbon chain include: alkyl groups, such as hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl,

hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, heneicosyl, docosyl, tricosyl, tetracosyl, heptacosyl, octacosyl, nonacosyl and triacetyl; and alkenyl groups, such as hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, octadecenyl, nonadecenyl, icosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, hexacosenyl, heptacosenyl, octacosenyl, nonacosenyl and triacentenyl.

The above alkyl and alkenyl groups include all possible straight structures or branched structures. Additionally, the position of double bonds in alkenyl groups is free.

[0058] The aliphatic amine compound can be exemplified by various amine compounds and derivatives of these, such as the nitrogen-L containing heterocyclic compounds of monoamine, polyamine, alkanolamine, imidazoline compound and the like each having straight or branched aliphatic hydrocarbon group having the carbon number of 6 to 30.

Monoamine can be concretely exemplified by laurylamine, L lauryldimethylamine, palmitylamine, stearylamine, L oleylamine and the like.

Polyamine can be concretely exemplified by stearyltetraethylenepentamine, oleylpropylenediamine and the like.

Alkanolamine can be concretely exemplified by lauryldiethanolamine, dodecyl/dipropanolamine, oleyldiethanolamine and the like.

The nitrogen-L containing heterocyclic compounds are concretely exemplified by N-L hydroxyethyloleylimidazoline and the like.

The derivatives are exemplified by alkylene oxide adducts, acid-L modified compounds and the like.

The alkylene oxide adducts are exemplified by compounds which are obtained upon addition of alkylene oxide to nitrogen oxide in the above-L mentioned various amine compounds, concretely by N, L-N-L dipolyoxyalkylene-L-N-L alkyl L (alkenyl) L amines which are obtained upon addition of alkylene oxide to primary monoamine having alkylene group and alkenyl group each having the carbon number of 6 to 28, more concretely

N, L-N-L dipolyoxyalkylene-L-N-L oleylamines and the like.

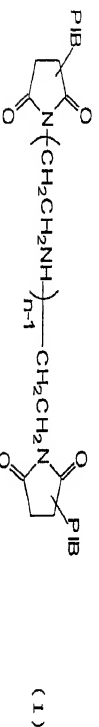
The acid-L modified compounds are exemplified by compounds prepared by reacting the above various amine compounds with carboxylic acids (II), preferably the above-L mentioned aliphatic monocarboxylic acids (II-L 1) (more preferably ones having the carbon number of 2 to 30), the above-L mentioned aliphatic polycarboxylic acids (II-L 2) (more preferably ones having the carbon number of 2 to 30, or containing oxalic acid or the like), the above-L mentioned carbonocyclic carboxylic acids (II-L 3) L (more preferably ones having the carbon number of 6 to 30, or containing phthalic acid, trimellitic acid and pyromellitic acid or the like) so as to neutralize or amidate the whole or part of the remaining amino and/or imino groups.

[0059] The contained amount of the oxygen-L containing organic compound or the aliphatic amine compound is not particularly restricted; however, the lower limit of the contained amount based on the total amount (total mass) of the low-L friction agent composition is normally 0.001 %, preferably 0.05 %, morepreferably 0.1%, particularly preferably

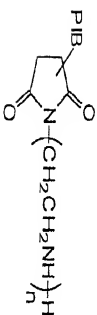
[0060] On the other hand, the lubricating oil for a manual transmission advantageously contains polybutenylsuccinimide or a derivative thereof.

The above-L mentioned polybutenyl succinimide include compounds represented by the following chemical formulas (1) and (2).

[0061]



[0062]



(2)

PIB in these chemical formulae represents a polybutenyl group derived from polybutene. The polybutene can be prepared by polymerizing high-purity isobutene or a mixture of 1-butene and isobutene in the presence of a boron fluoride catalyst or an aluminum chloride catalyst in such a manner that the polybutene attains a number-average molecular weight of 900 to 3,500, preferably 1,000 to 2,000. When the number-average molecular weight of the polybutene is less than 900, there is a possibility of failing to attain a sufficient detergent effect. When the number-average molecular weight of the polybutene exceeds 3,500, the polybutene may undesirably deteriorate in low-temperature fluidity.

In each of the chemical formulae, n represents an integer of 1 to 5, preferably 2 to 4, so as to attain a good detergent effect. In the production of the polybutenyl succinimide, the polybutene may be used after purified by removing trace amounts of fluorine and chlorine residues, which result from the above polybutene production catalyst, by any suitable treatment (such as adsorption process or washing process). The amount of the fluorine and chlorine residues is preferably controlled to 50 ppm or less, more preferably 10 ppm or less, most preferably 1 ppm or less.

[0063] The production method of the polybutenyl succinimide is not particularly restricted. For example, the polybutenyl succinimide can be prepared by reacting an chloride of the above-mentioned polybutene, or the polybutene from which fluorine and chlorine residues are removed, with maleic anhydride at 100 to 200°C to form polybutenyl succinate, and then, reacting the thus-formed polybutenyl succinate with polyamine (such as diethylene triamine, triethylene tetramine, tetraethylene pentamine or pentaethylene hexamine).

[0064] The polybutenyl succinimide derivative can be exemplified by boron- and acid-modified compounds obtained by reacting the polybutenyl succinimide of

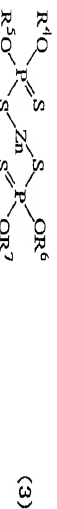
the formulas (1) and (2) with boron compounds or oxygen-^L-containing organic compounds so as to neutralize or amidate the whole or part of the remaining amino and/or imide groups. Among these, boron-^L-containing polybutenyl succinimide, especially boron-^L-containing bis-^L (polybutenyl)^L succinimide, is preferably used.

[0065] The above boron compound can be a boric acid, a borate or a boric acid ester. Specific examples of the boric acid include orthoboric acid, metaboric acid and paraboric acid. Specific examples of the borate include: ammonium salts including ammonium borates, such as ammonium metaborate, ammonium tetraborate, ammonium pentaborate and ammonium octaborate. Specific examples of the boric acid ester include: esters of boric acids and alkylalcohols (preferably C1-C6 alkylalcohols), such as monomethyl borate, dimethyl borate, trimethyl borate, monoethyl borate, diethyl borate, triethyl borate, monopropyl borate, dipropyl borate, tripropyl borate, monobutyl borate, dibutyl borate and tributyl borate. Herein, the content ratio of nitrogen to boron (B/N) by mass in the boron-^L-containing polybutenyl succinimide is usually 0.1 to 3, preferably 0.2 to 1.

¹. The above oxygen-^L-containing organic compound can be exemplified by: C1-C30 monocarboxylic acids, such as formic acid, acetic acid, glycolic acid, propionic acid, lactic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, oleic acid, nonadecanoic acid and eicosanoic acid; C2-C30 polycarboxylic acids, such as oxalic acid, phthalic acid, trimellitic acid and pyromellitic acid, and anhydrides and esters thereof; C2-C6 alkylene oxides; and hydroxy-^L (poly)^L oxyalkylene carbonates.

[0066] The amount of the polybutenyl succinimide and/or the derivative thereof added in the low-^L-friction agent composition is not particularly restricted, and is preferably 0.1 to 15%, more preferably 1.0 to 12%, based on the total amount of the lubricating oil. When the amount of the polybutenyl succinimide and/or the derivative thereof is less than 0.1%, there arises a possibility of failing to attain a sufficient detergent effect. It becomes uneconomical when the amount of the polybutenyl succinimide and/or the derivative thereof exceeds 15%. In addition, such a large amount of the polybutenyl succinimide and/or the derivative thereof tends to cause a deterioration in demulsification ability. [0067] Further, the lubricating oil composition used for the present invention

preferably contains zinc dithiophosphate expressed by the following expression (3).
[0068]



In the chemical formula (3), R⁴, R⁵, R⁶ and R⁷ each represent C1-C24 hydrocarbon groups. The C1-C24 hydrocarbon group is preferably a C1-C24 straight-L-chain or branched-L-chain alkyl group, a C3-C24 straight-L-chain or branchedchain alkenyl group, a C5-C13 cycloalkyl or straight-L-chain or branched-L-chain alkylcycloalkyl group, a C6-C18 aryl or straight-L-chain or branched-L-chain alkylaryl group, or a C7-C19 arylalkyl group. The above alkyl group or alkenyl group can be primary, secondary or tertiary.

[0069] Specific examples of R⁴, R⁵, R⁶ and R⁷ include: alkyl groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, heneicosyl, docosyl, tricosyl and tetracosyl; alkenyl groups, such as propenyl, isopropenyl, butenyl, butadienyl,

pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl,

hexadecenyl, heptadecenyl, octadecenyl (oleyl), nonadecenyl, icosenyl, heneicosenyl, docosenyl, tricosenyl and tetracosenyl;

cycloalkyl groups, such as cyclopentyl, cyclohexyl and cycloheptyl; alkylcycloalkyl groups, such as methylcyclopentyl,

dimethylcyclopentyl, ethylcyclopentyl, propylcyclopentyl, ethylmethylcyclopentyl, trimethylcyclopentyl, diethylcyclopentyl,

L ethyldimethylcyclopentyl, propylmethylcyclopentyl, propylethylcyclopentyl, di-L propylcyclopentyl, propyl

ethylmethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, ethylcyclohexyl,

propylcyclohexyl, ethyl/methylcyclohexyl, ethyldimethylcyclohexyl, trimethylcyclohexyl, diethylcyclohexyl, ethylcyclohexyl, propylmethylcyclohexyl, propylethylcyclohexyl, di-^L propylcyclohexyl, propylethylmethylcyclohexyl, methylcycloheptyl, dimethylcycloheptyl, ethylcycloheptyl, propylcycloheptyl, ethylmethylcycloheptyl, trimethylcycloheptyl, diethylcycloheptyl, ethyldimethylcycloheptyl, propylethylmethylcycloheptyl, propylethylcycloheptyl, di-^L propylcycloheptyl and propylethylmethylcycloheptyl; aryl groups, such as phenyl and naphthyl; alkylaryl groups, such as tolyl, xylyl, ethylphenyl, propylphenyl, ethylmethylphenyl, trimethylphenyl, butylphenyl, propylmethylphenyl, diethylphenyl, ethyldimethylphenyl, tetramethylphenyl, pentylphenyl, hexylphenyl, heptylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl and dodecylphenyl; and arylalkyl groups, such as benzyl, methylbenzyl, dimethylbenzyl, phenethyl, methylphenethyl and dimethylphenethyl.

The above-^L mentioned hydrocarbon groups include all considerable straight or branched chain structures. The position of double bond of alkenyl group, the bonding position of alkyl group to cycloalkyl group and the bonding position of alkyl group to aryl group are free.

[0070] Specific examples of the zinc dithiophosphate usable include zinc diisopropylidithiophosphate, zinc diisobutylidithiophosphate, zinc di-^L sec-^L butylidithiophosphate, zinc di-^L sec-^L pentylidithiophosphate, zinc di-^L n-^L hexyldithiophosphate, zinc di-^L sec-^L hexyldithiophosphate, zinc di-^L octyldithiophosphate, zinc di-^L 2-^L ethylhexyldithiophosphate, zinc di-^L n-decylidithiophosphate, ^L zinc di-^L n-^L dodecylidithiophosphate, zinc diisotridecylidithiophosphate and mixtures thereof.

[0071] The amount of the zinc dithiophosphate added in the lubricating oil is not particularly restricted. The zinc dithiophosphate is preferably contained in an amount of 0.1% or less, more preferably in an amount of 0.06% or less, most preferably in a minimum effective amount, in terms of the phosphorus element based on the total amount of the lubricating oil in order to produce a higher friction reducing effect. When the amount of the zinc dithiophosphate exceeds 0.1%, there arises a possibility of inhibiting the excellent friction reduction effect of the oxygen-^L containing organic compound (C) at sliding surfaces of the DLC member and various metal materials, particularly iron-^L based material.

[0072] The zinc dithiophosphate can be prepared by any known method. For example, the zinc dithiophosphate may be prepared by reacting alcohols or phenols having the above R4, R5, R6 and R7 hydrocarbon groups with phosphorous pentasulfide to form dithiophosphoric acid, and then, neutralizing the thus-formed dithiophosphoric acid with zinc oxide. Herein, the molecular structure of zinc dithiophosphate differs according to the alcohols and the like used as a raw material for the zinc dithiophosphate production.

The other anti-friction agent or extreme-pressure additive can be exemplified by disulfides, sulfurized fats and oils, olefin sulfides, phosphate esters having one to three C2-C20 hydrocarbon groups, thiophosphate esters, phosphate esters, thiophosphate esters and amine salts of these esters.

[0073] As described above, in a case where the lubricating oil for a manual transmission used in the present invention is used in the sliding surface to the hard carbon thin film such as DLC, it shows extremely excellent low friction characteristics, but, for enhancing the performance necessary as the working oil of a transmission particularly, metallic cleaner, anti-oxidizing agent, viscosity index improver, the other ashless friction modifier, the other ashless disperser, anti-wear agent or an extreme pressure agent, an anti-rust agent, non-ion surface active agent, an anti-embulsifier, a metallic inactive agent, a defoamer or the like is used alone or combined, making it possible to increase the necessary performance.

[0074] The metallic detergent can be any metallic-L detergent compound commonly used for a lubricating oil. Specific examples of the metallic detergent usable in connection with the present invention include sulfonates, phenates and salicylates of alkali metals or alkali-L earth metals; and mixtures of two or more thereof. Examples of the alkali metals include sodium (Na) and potassium (K), and examples of the alkali-L earth metals include calcium (Ca) and magnesium (Mg). In connection with the present invention, sodium and calcium sulfonates, sodium and calcium phenates, and sodium and calcium salicylates are suitably used. The total base number and amount of the metallic detergent can be selected in accordance with the lubricating oil performance required. The total base number of the metallic detergent is usually 0 to 500 mgKOH/g, preferably 150 to 400 mgKOH/g, as measured by perchloric acid method according to ISO 3771 "Determination of base number - Perchloric acid potentiometric titration method". The amount of the metallic detergent is usually 0.1 to 10% based on the total amount of the lubricating oil.

[0075] The antioxidant can be any antioxidant compound commonly used for a lubricating oil. Specific examples of the antioxidant usable in connection with the present invention include: phenolic antioxidants, such as 4,4'-methylenebis (2,6-di-tert-butylphenol) and octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate; amino antioxidants, such as phenyl-a-naphthylamine, alkylphenyl-a-naphthylamine and alkylidiphenylamine; and mixtures of two or more thereof.

The amount of the antioxidant is usually 0.01 to 5% based on the total amount of the lubricating oil.

[0076] The viscosity index improver can be concretely exemplified by: non-dispersion type viscosity index improvers, such as copolymers of one or two monomers selected from various methacrylic acids, and hydrides of the copolymers; and dispersion type viscosity index improvers, such as copolymers of methacrylates (including nitrogen compounds).

There may be also used, as the viscosity index improver, copolymers of ethylene and α -olefins (such as propylene, 1-butene and 1-pentene) and hydrides thereof, polyisobutylenes and hydrides thereof, a hydrogenated copolymer of styrene and diene, a copolymer of styrene and maleic anhydride and polyalkylenes.

The molecular weight of the viscosity index improver needs to be selected in view of shear stability. For example,

the number-average molecular weight of the viscosity index improver is desirably in a range of 5,000 to 1,000,000, more desirably 100,000 to 800,000, for dispersion or non-dispersion type polymethacrylates; in a range of 800 to 5,000 for polyisobutylenes and hydrides thereof; and in a range of 800 to 300,000, more desirably 10,000 to 200,000 for ethylene/ α -olefin copolymers and hydrides thereof. The above viscosity index improving compounds can be used alone or in the form of a mixture of two or more thereof. The amount of the viscosity index improver is preferably 0.1 to 40.0% based on the total amount of the lubricating oil.

[0077] The other friction modifier can be exemplified by metallic friction modifier such as ashless friction modifier such as boric acid ester, higher alcohol, and fatty ester, molybdenum dithiophosphate, molybdenum dithiocarbamate, molybdenum disulfide and the like.

The ashless dispersant other than the above-mentioned can be exemplified by

polybutenylbenzylamines and polybutenylamines each having polybutenyl groups of number-average molecular weight of 900 to 3,500, polybutenyl succinimides having polybutenyl groups of number-average molecular weight of less than 900 and derivatives thereof.

[0078] Further, examples of the anti-wear agent or the extreme pressure agent include disulfide, sulfide fat, sulfide olefin, phosphoric ester containing 1 to 3 pieces of hydrocarbon group of C2 to C20, thiophosphoric ester, phosphorous acid ester, thiophosphorous acid ester and amine salt thereof.

Further, the rust inhibitor can be exemplified by alkylbenzene sulfonates, dinonylnaphthalene sulfonates, esters of alkenylsuccinic acids and esters of polyhydric alcohols.

[0079] The nonionic surfactant and the demulsifier can be exemplified by nonionic polyalkylene glycol surfactants, such as polyoxyethylene alkylethers, polyoxyethylene alkylphenylethers and polyoxyethylene alkylnaphthylethers.

The metal deactivator can be exemplified by imidazoline, pyrimidine derivatives, thiazol, benzotriazole, thiadiazole and the like.

The anti-foaming agent can be exemplified by silicones, fluorosilicones and fluoroalkylethers.

[0080] In case that these additives are contained in the low-friction agent composition used in the present invention,

the contents of them are as follows: The friction modifier other than (C) and (D), the content of the rust inhibitor and

demulsifier can be suitably selected from the range of 0.01 to 5% based on the total amount of the composition; and the content of the metal deactivator can be suitably selected from the range of 0.0005 to 1% based on the total amount of the composition.

[0081]

[EXAMPLE]

Hereinafter, the present invention will be in more detail explained with reference to examples and comparative example, but the present invention is not limited to these examples.

[0082]

As shown in Fig. 2, a cylinder side test piece 11 as a sliding-side test piece and a disc-like test piece 12 as an opponent side test piece were used to conduct a friction test of a single cylinder-on disc reciprocating movement, where the friction coefficient was measured under the following condition.

[1] Friction Test Conditions

Test device: Cylinder-on-disc reciprocating friction tester

Sliding side test piece: $\phi 15 \times 22$ mm cylinder-L like test piece

Counterpart side test piece: $\phi 24 \times 7.9$ mm disc-L like test piece

Load: 400N (pressing load of the sliding side test piece)

Amplitude: 3.0 mm

Frequency: 50Hz

Test temperature: 80°C

Measurement time period: 30 min

[0083] [2] Preparation of cylinder-like test piece (sliding side)

With SUJ2 steel stipulated as high-carbon chromium bearing steel in JIS G4805 as a raw material, a cylinder-like test piece 11 that is a sliding side test piece was machined into the above dimension, followed by finishing to the surface roughness Ra of 0.04 μ m.

[0084] [3] Preparation of disc-like test piece (sliding counterpart side)

Similarly, with SUJ2 steel, a disc-L like test piece 12 that is a counterpart side test piece was machined to the dimension, after an upper sliding surface was finished to the surface roughness Ra of 0.05 μ m, by means of a PVD arc ion type ion plating process, on a surface thereof, a DLC thin film where an amount of hydrogen atoms is 0.5 atomic percent or less, the Knoop hardness HK is 2170 kg/mm², and the surface roughness Ry is 0.03 μ m was deposited at a film thickness of 0.5 μ m. In the Reference Example, one that was not coated with the DLC thin film was used.

[0085]

[4] Preparation of low-friction agent composition for use in manual transmission

As a low-friction agent composition for use in a manual transmission, ones where to mineral oil or synthetic oil (PAO: poly- α -olefin (1-octene oligomer)) as base oil, SP (S and P-containing compound with 0.5% by mass of an amine salt of thiophosphoric acid) or ZnDTP (zinc dithiophosphate) extreme pressure agent (1.5% by mass as a compound), the wear resistance agent and an aliphatic ester or aliphatic amine friction modifier were respectively combined were prepared.

[0086]

[5] Test results

The cylinder-like test pieces and disc-like test pieces, and the low-friction agent compositions for use in the manual transmission were combined as shown in

Table 1, followed by measuring the friction coefficients according to a procedure shown above. Results are shown in Fig. 3.
[0087]

Table 1

Division	Disc-like test piece		Raw material of cylinder-like test piece	Low-friction agent composition for manual transmission		
	Raw material (DLC thin film)	Hydrogen content (at%)		Base oil	Extreme pressure agent/wear resistant agent	Friction modifier
Example 1	SUJ2 (Yes)	0.5	SUJ2	Mineral oil	SP+ZnOTP system	Fatty ester
Example 2	SUJ2 (Yes)	0.5	SUJ2	Mineral oil	SP system	Fatty ester
Example 3	SUJ2 (Yes)	0.5	SUJ2	Mineral oil	SP+ZnOTP system	Aliphatic amine
Example 4	SUJ2 (Yes)	0.5	SUJ2	Mineral oil	SP system	Aliphatic amine
Example 5	SUJ2 (Yes)	0.5	SUJ2	PAO	SP+ZnOTP system	Fatty ester
Example 6	SUJ2 (Yes)	0.5	SUJ2	PAO	SP system	Fatty ester
Example 7	SUJ2 (Yes)	0.5	SUJ2	PAO	SP+ZnOTP system	Aliphatic amine
Example 8	SUJ2 (Yes)	0.5	SUJ2	PAO	SP system	Aliphatic amine
Comparative Example 1	SUJ2 (No)	-	SUJ2	Mineral oil	SP+ZnOTP system	Fatty ester
Comparative Example 2	SUJ2 (No)	-	SUJ2	Mineral oil	SP system	Fatty ester
Comparative Example 3	SUJ2 (No)	-	SUJ2	Mineral oil	SP+ZnOTP system	Aliphatic amine
Comparative Example 4	SUJ2 (No)	-	SUJ2	Mineral oil	SP system	Aliphatic amine
Comparative	SUJ2	-	SUJ2	PAO	SP+ZnOTP	Fatty

Example 5	(No)		SUJ2	PAO	system	ester
Comparative Example 6	SUJ2 (No)	-			SP system	Fatty ester
Comparative Example 7	SUJ2 (No)	-	SUJ2	PAO	SP+ZnOTP system	Aliphatic amine
Comparative Example 8	SUJ2 (No)	-	SUJ2	PAO	SP system	Aliphatic amine

[00088] As obvious from results of Fig. 3, it was confirmed that in examples where a disc-like test piece on an upper sliding surface of which a DLC thin film was deposited was used, in comparison with Comparative Examples where a disc-like test piece on which a DLC thin film was not deposited was used, the friction coefficient was largely lowered.

[00089]

[EFFECT OF THE INVENTION]

As described above, according to the present invention, at least one of the sliding surfaces in the sliding portion in the manual transmission under the existence of the lubricating oil for the manual transmission is coated with the hard carbon thin film having a few hydrogen content, and therefore, anti-wear properties and anti-seizure properties can be improved in the sliding portion in the manual transmission and also a fuel economy performance for an automobile can be improved by reducing the friction coefficient and the sliding resistance.

[BRIEF DESCRIPTION OF THE DRAWINGS]

Fig. 1 is a cross sectional explanatory diagram illustrating a sliding portion coated with a hard carbon thin film in the manual transmission.

Fig. 2 is a perspective view showing a procedure of a cylinder-on-disc reciprocating dynamic friction test that is used in a friction test in examples in the present invention.

Fig. 3 is a graph showing the result by comparing friction coefficients by a cylinder-on-disc reciprocating dynamic friction test shown in Fig. 2.

[DESCRIPTION OF THE CODES]

1: MANUAL TRANSMISSION

2c THIRD SPEED NEEDLE BEARING (SLIDING PORTION)

2d FOURTH SPEED NEEDLE BEARING (SLIDING PORTION)

3 INPUT SHAFT (SLIDING PORTION)

4c FIRST SPEED NEEDLE BEARING (SLIDING PORTION)
4d SECOND SPEED NEEDLE BEARING (SLIDING PORTION)
5 MAIN SHAFT
6a SECOND SPEED BUSH (SLIDING PORTION)
6b FIFTH SPEED BUSH (SLIDING PORTION)

[DOCUMENT TITLE] DRAWINGS

Fig. 1

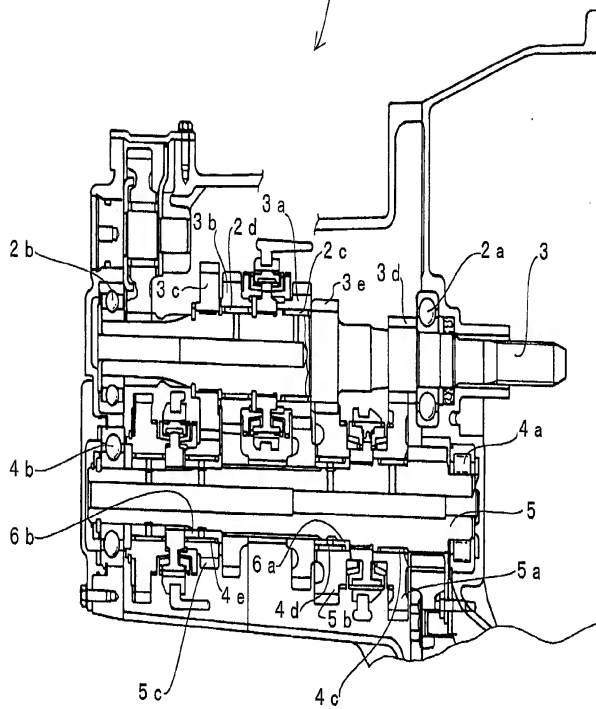
手動變速機: MANUAL TRANSMISSION

【書類名】

図面

【図 1】

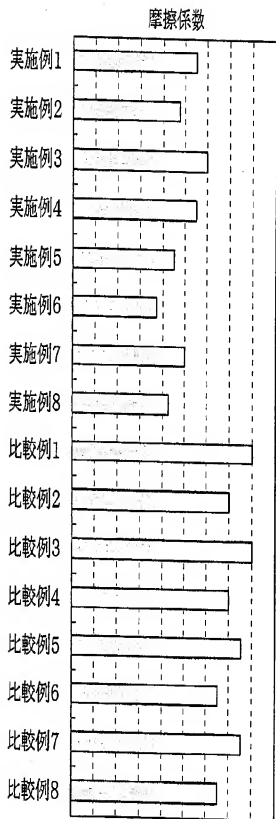
1 手動変速機



【图 2】



Fig. 3
 摩擦係數: FRICTION COEFFICIENT
 實施例: EXAMPLE
 比較例: COMPARATIVE EXAMPLE
 【圖 3】



[DOCUMENT TITLE] ABSTRACT

[ABSTRACT]

[PROBLEM]

Provided is a manual transmission that can reduce the friction coefficient in various kinds of sliding sections such as the in the manual transmission to improve the seizure resistance and the wear resistance and to reduce the sliding resistance of the respective sections to contribute in improving the fuel efficiency of an automobile.

[MEANS FOR THE SOLUTION]

One or both of sliding surfaces sliding with each other under existence of the lubricating oil for the final gear reduction unit is coated with a hard carbon thin film having the low hydrogen content, such as diamond-like carbon.

[SELECTIVE DRAWING] Fig. 1